Resolution Limits in EUV resists

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Outline – Resolution Limitations in CA resists

- Introduction
- History
- Routes to High resolution CA EUV resists
  - Low Ea resists
  - Bound PAGs
  - AI Shaping
  - Other sources of image blur
  - Inorganic resists
- Summary

Introduction

- Recent overviews of the status of EUV resist development
  - SPIE 2011 Resist Keynote Talks
    - Critical challenges for EUV resist materials P. Naulleau et al (LBNL)
    - Materials challenges for sub-20nm lithography J. W. Thackeray (Dow Electronic Chemicals)
- RLS Challenges
- Goal of this presentation – Confine the discussion to the resolution limitations of CA Resists

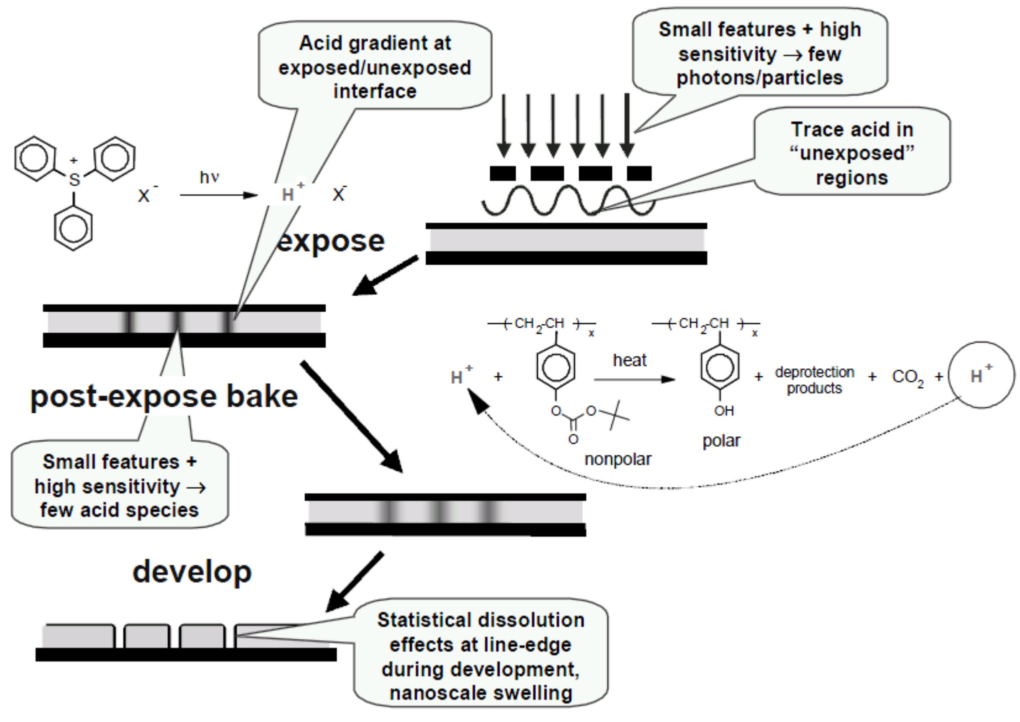


Figure 3. Origins of limiting factors in CA resists.

Hinsberg et al SPIE 2003

Image Blur (Acid Diffusion) History

TBOC - First CA resist used in semiconductor manufacturing

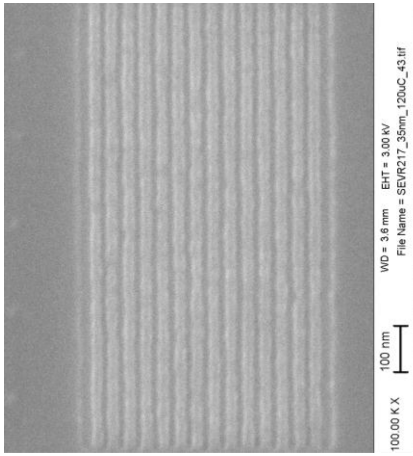
Nanolithography with a high resolution STEM

Umbach, Broers, Koch, Willson, Laibowitz IBM J. Res Develop. 1988

"This latter result indicates not only that the PC XT-driven STEM is producing reliable exposure distribution data, but also that t-BOC has approximately the same resolution as PMMA, even though its sensitivity can be six times higher. These results suggest that resolution may be limited by something inherent in all organic resists, such as, perhaps, the range over which low-energy secondary electrons are created by high-energy electrons"

TBOC resist (no base additive) NTD - solvent anisole. Used to manufacture 1 Mbit DRAM (1 micron feature size)

CA Resist 35 nm Pitch, 20 nm line, SEVR 217



J. Bucchignano, K. Petrillo, M. Guillorn IBM

Examples - High Resolution E Beam

- E beam
  - CA – 20 nm (15 nm)
  - Non CA
    - HSQ – 5 nm (MIT)
    - PMMA - 8 nm
    - Inorganic – 2 nm (NaCl)

PMMA

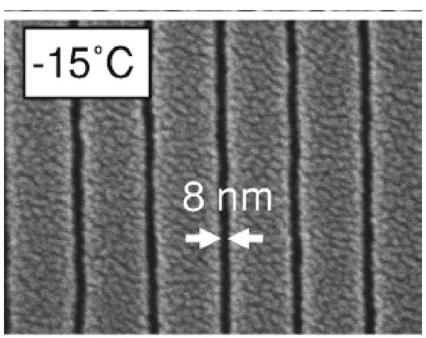
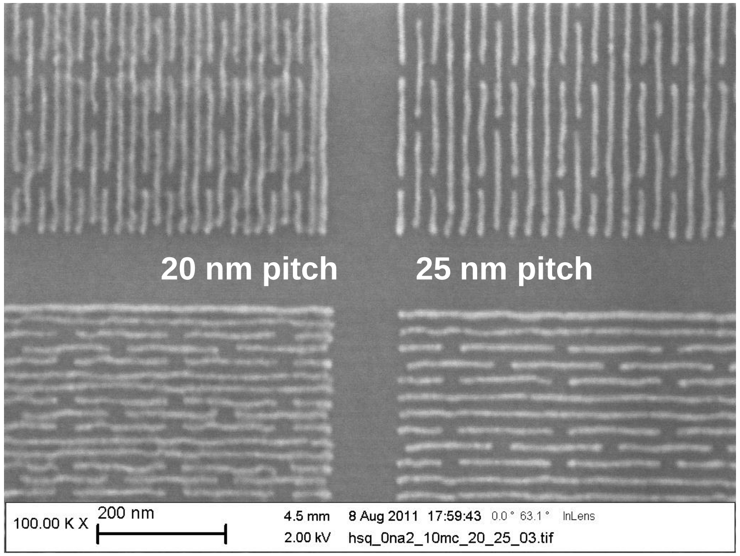


FIG. 4. SEM images of 60 nm pitch gratings developed in 3:1 IPA:MIBK for 30 s at 15, 0, −15, and −30 °C and etched into a Si substrate, showing the minimum achievable linewidth at each development temperature. As expected from the contrast data, the resolution improves as the temperature is reduced, peaks at −15 °C, and then drops sharply at −30 °C. The poor line-edge definition and bridging in the −30 °C micrograph are characteristic of sloped resist sidewalls, a symptom of poor resist contrast.

B. Cord,J Lutkenhaus, K Berggren JVST 2007

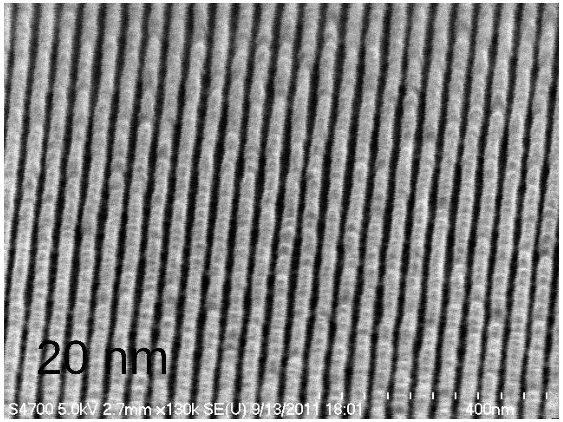
HSQ



E. Kratschmer IBM

Examples of High resolution EUV

- EUV
  - CA – 18 - 20 nm (many examples)
  - Non CA
    - HSQ – 11 nm (PSI)
    - Calixarene – 12.5 nm PSI
    - Inorganic – 14 nm (LBNL Inpria)



110C/100C/60s, MF26A/45s, FT=40nm, 23.15mJ/cm2

P. Brock, H. Truong IBM

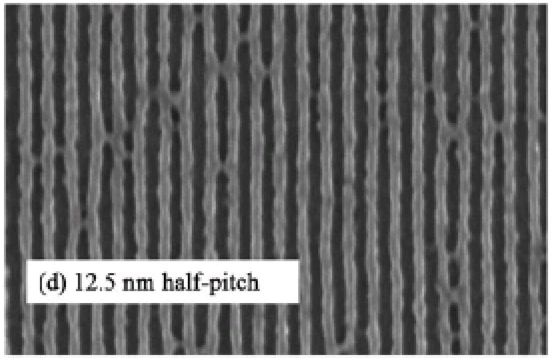
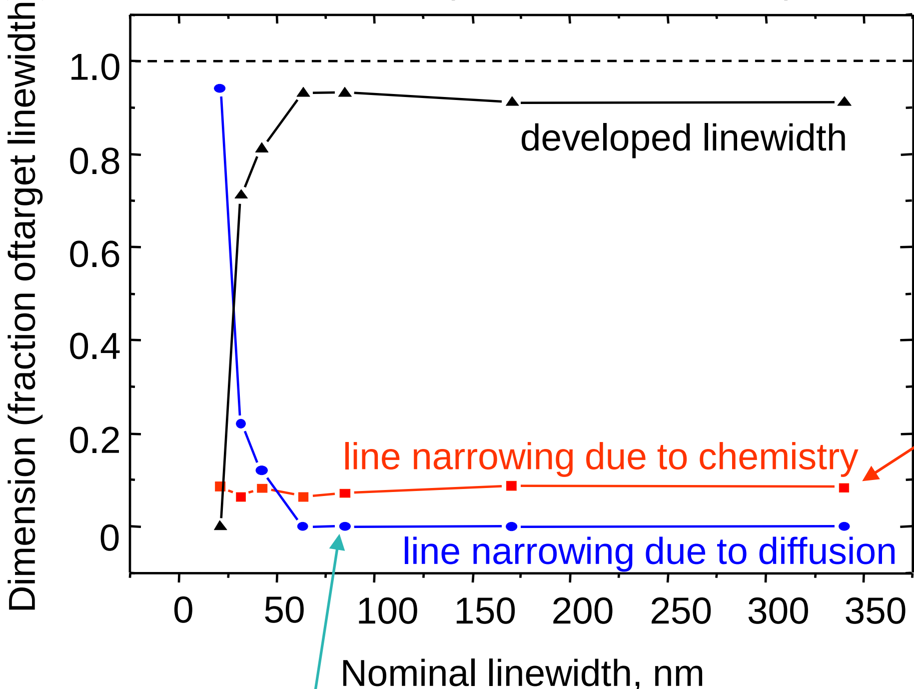


FIG. 2. Top-down SEM micrographs of IL generated line/space patterns in calixarene with half-pitches of a 20 nm, b 17.5 nm, c 16.25 nm, and d 12.5 nm.

Solak et al JVSTB 2007

Factors Affecting Intrinsic Resolution Limits in Chemically Amplified Resists

PFBS / PTBOCST, simple threshold development model



Deprotection in nominally unexposed areas near the line-edge, a consequence of small amounts of photogenerated acid produced by diffracted and scattered light, can lead to line narrowing that in many aspects mimics the effects of acid diffusion.

chemical contribution

…due to traces of acid in "unexposed" areas
...dominant contribution to image blur above 50 nm

…***increases*** with acid catalysis efficiency
…***increases*** with radiation dose
…***increases*** with uncatalyzed thermolysis rate
…***decreases*** with added base

diffusion contribution

...dominant contribution to image blur below 50 nm
...dramatic loss of resolution

…***increases*** with decreasing photoacid anion size
…***increases*** with increasing acid gradient (increased dose, decreased pitch
…***decreases*** with increasing polymer rigidity and polarity
…***decreases*** with added base

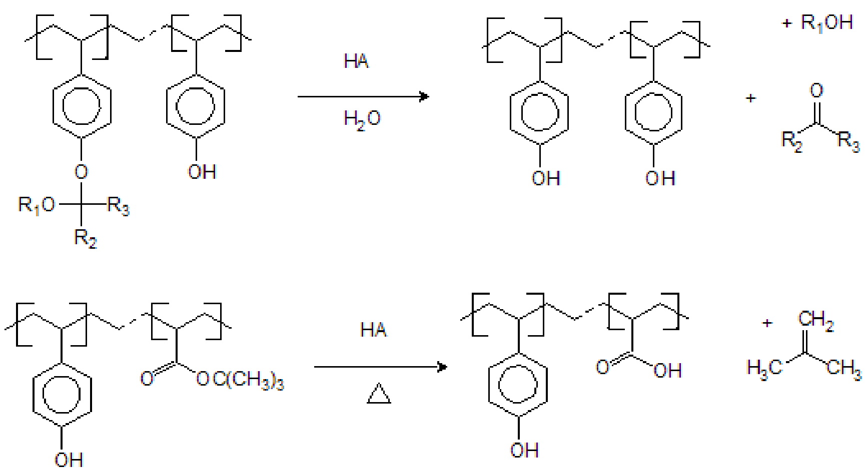
Hinsberg et al SPIE 2004

Control of Acid Diffusion

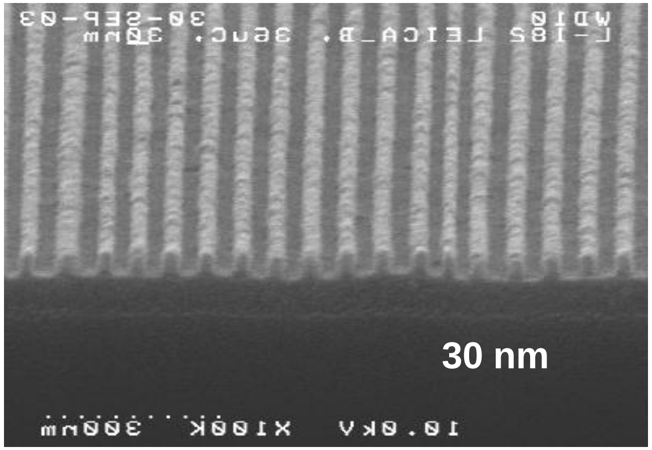
- Addition of Base quenchers
- Use of higher volume photoacid generators
- Low Ea resists that do not require a post expose bake
- Use of polymer bound PAG's

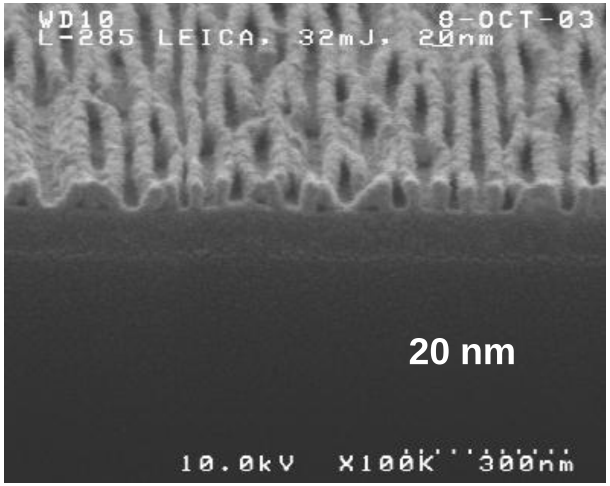
KRS Intro – No PEB Chemistry

KRS vs. ESCAP Chemistry – Wet and Cold vs. Hot and Dry



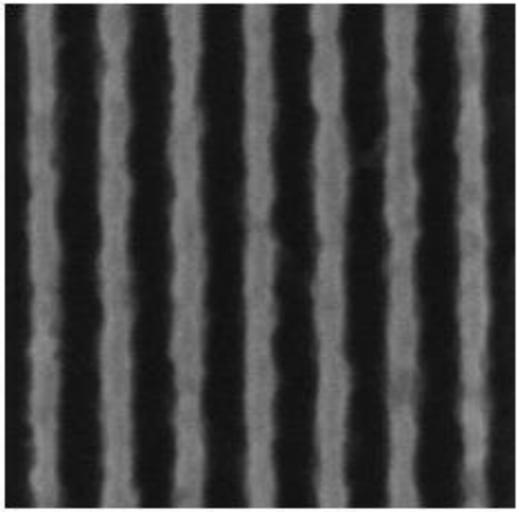
No Bake => No (Less) Blur



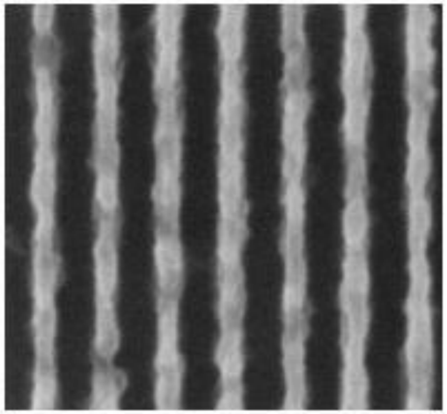


E Beam Exposures

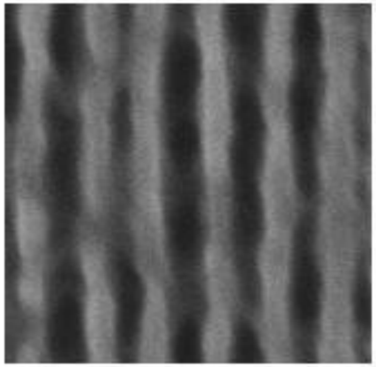
Low-activation-energy resists provide potential path to sub-25-nm EUV printing



28-nm lines, 70-nm pitch
LER = 4.6 nm



27-nm lines, 60-nm pitch
LER = 5.2 nm



25-nm
lines and spaces
LER = 10 nm

Data courtesy of
Greg Wallraff and Carl Larson, IBM

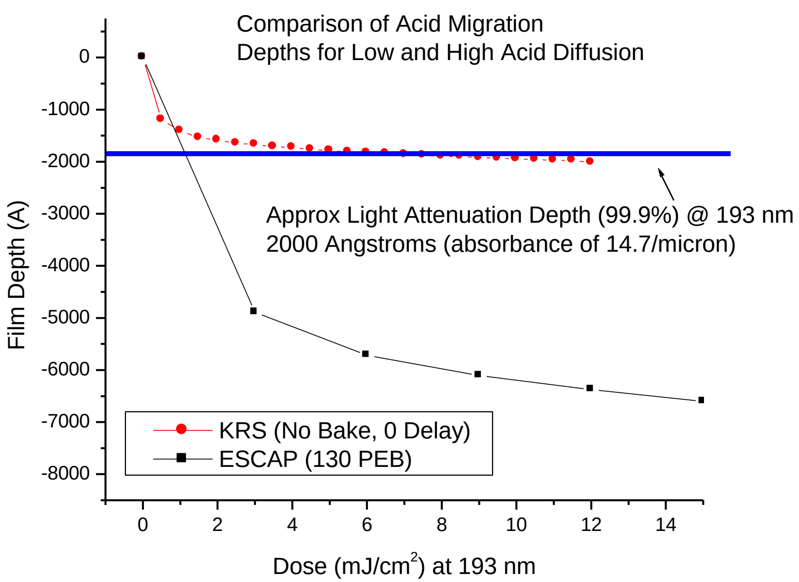
25-nm isolated line
LER = 4.6 nm

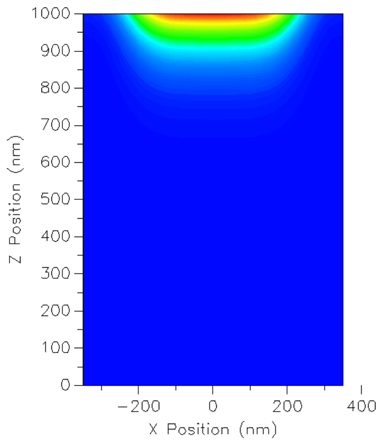
Patrick Naulleau

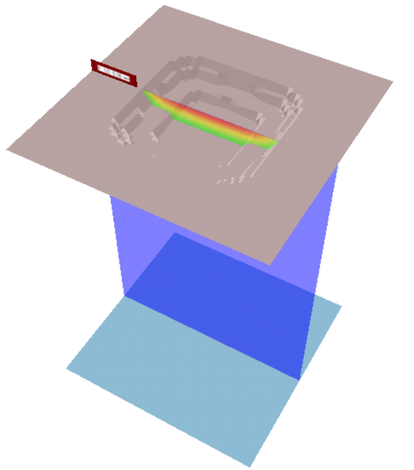
VNL EUVL Program Review, September 8th, 2004, Berkeley, California

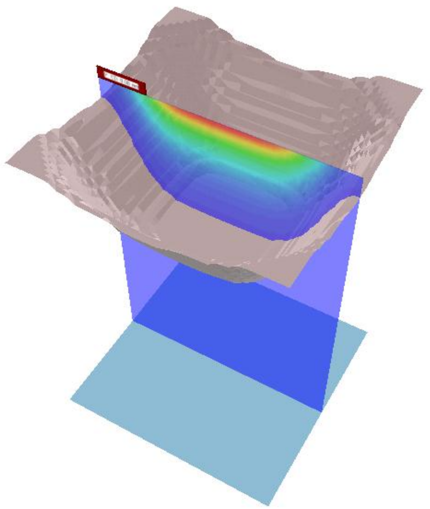
"1D" Technique for the Measurement of Chemical Image Blur

- Exposure of an optically opaque resist film - confinement of photoacid to thin surface layer
- Measurement of the extent of reaction (development depth) in the resist film as a function of imaging dose and temperature (convolution of diffusion and reactivity)







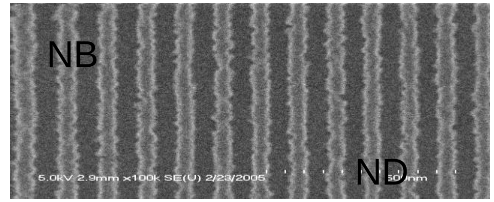


Similar to Bilayer Method (UT,NIST others)

No Bake Chemistry

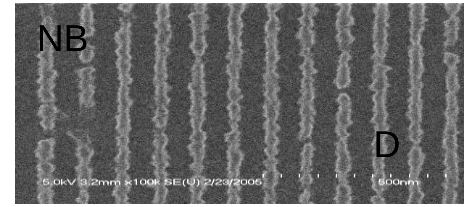
- What is the role of water in determining resist resolution ?

No Delay



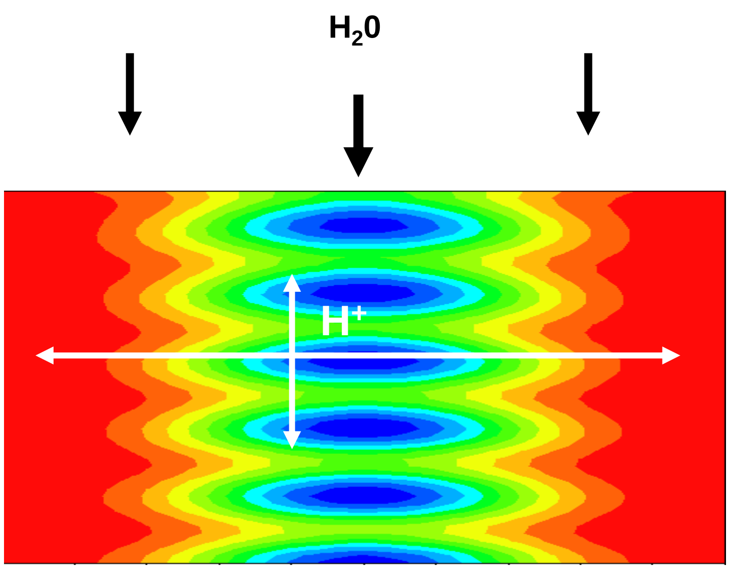
CD 50.8
LWR' 16.4
LER' 10.7

1 Hr Delay



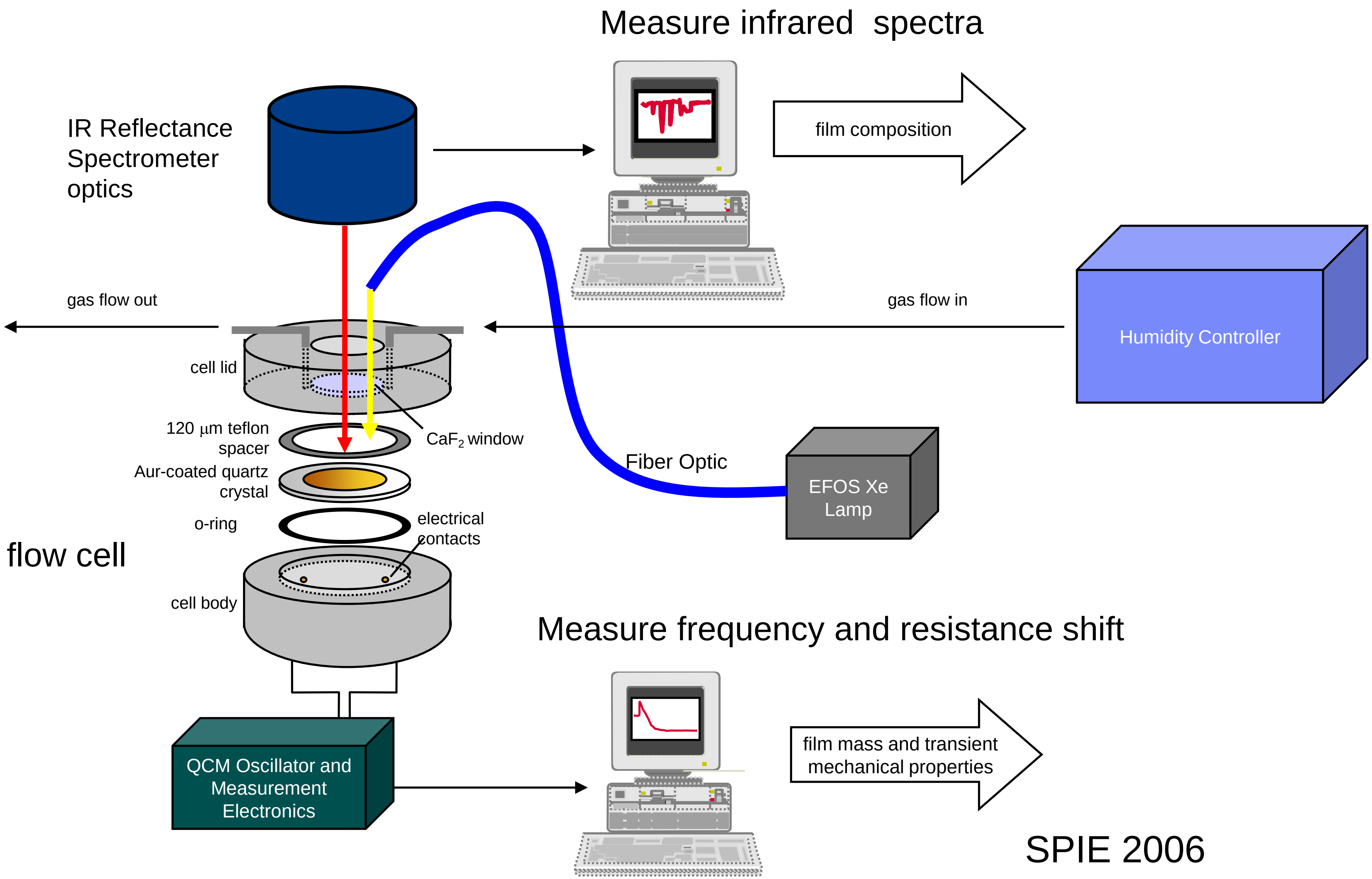
CD 39.2
LWR' 21.8
LER' 13.8

KRS E-Beam exposure/no base
nominal 100 nm pitch



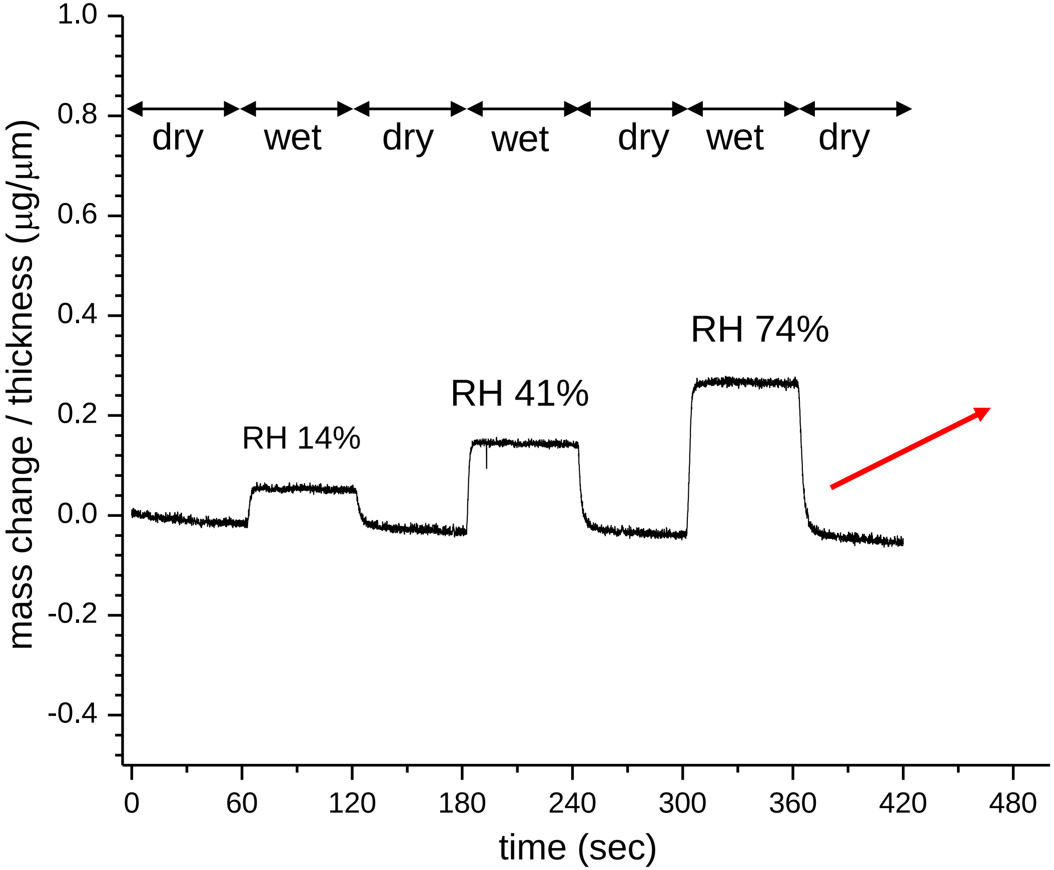
KRS 24 exposure 11 x 8 dose array no base

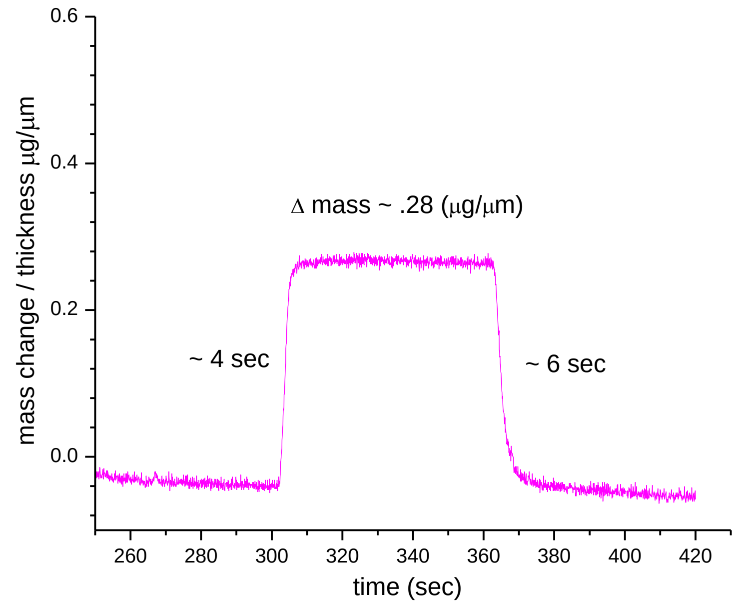
Diagram of QCM – IR – Exposure System



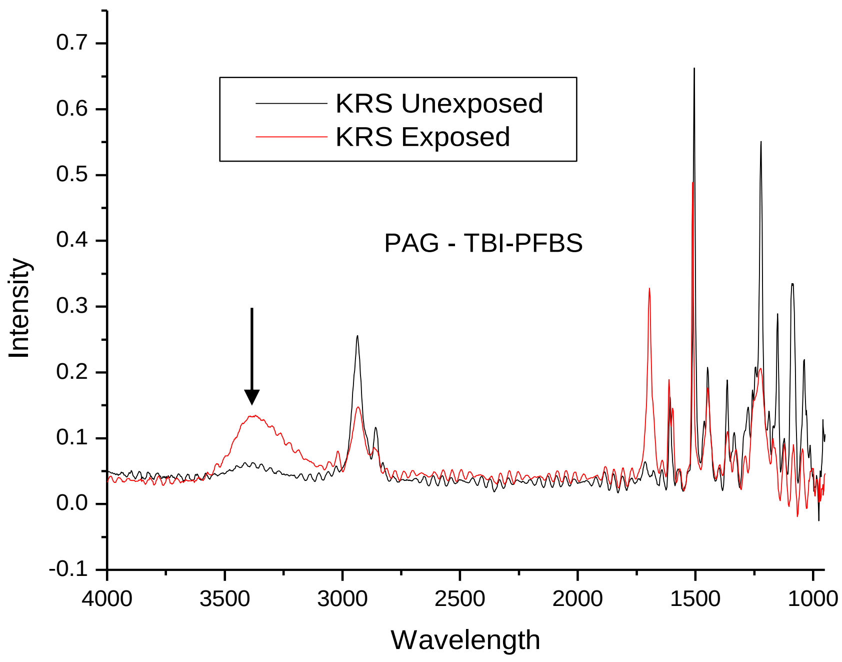
SPIE 2006

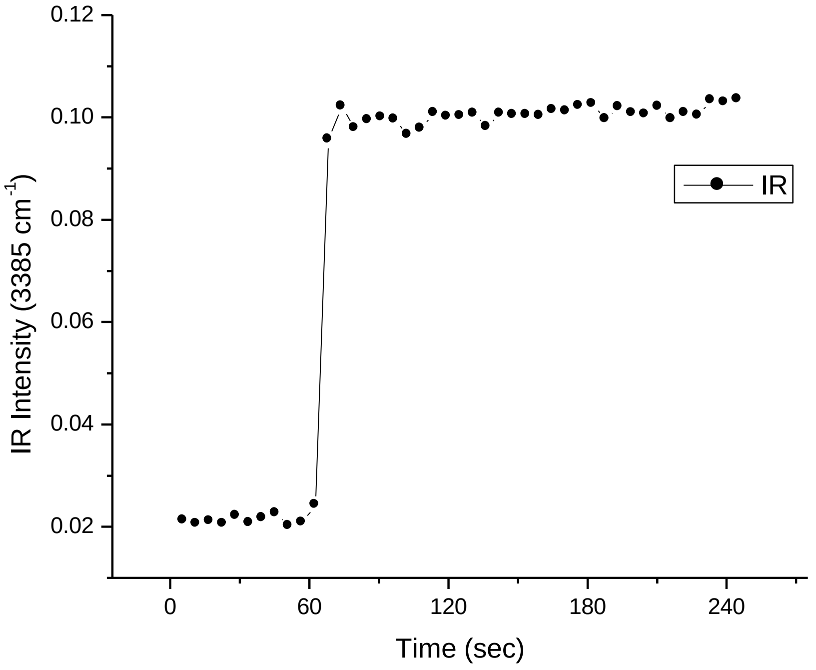
QCM - Time Response Vapor Phase Water Absorption – Unexposed KRS



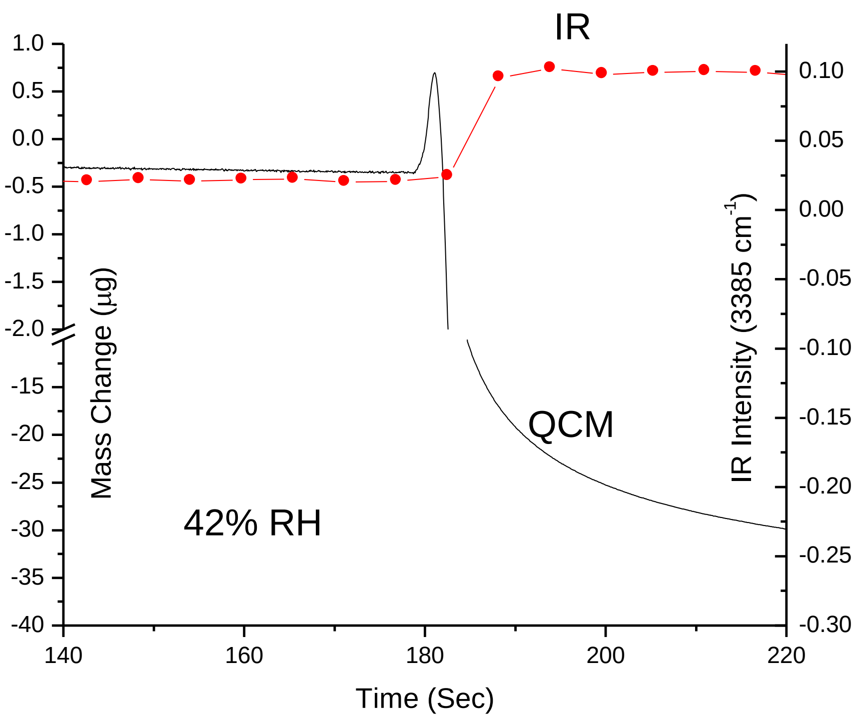


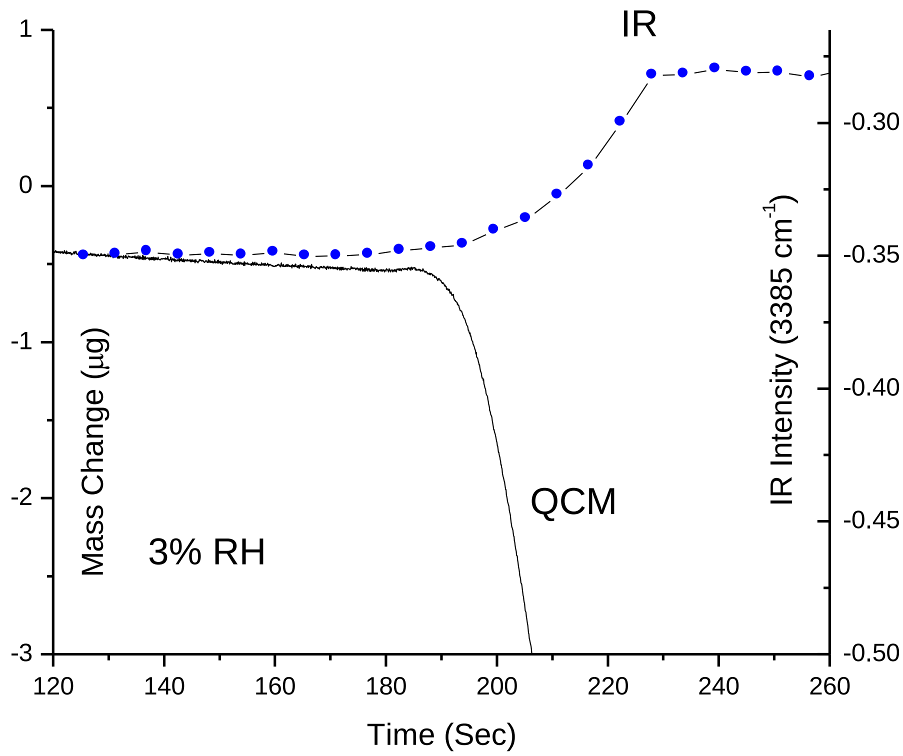
IR Measurement of KRS Deprotection





Dual QCM:IR - RH 42% and 3%





Conclusion – The rate of water absorption and deprotection occur on the same time scale

Summary – Low Ea resists

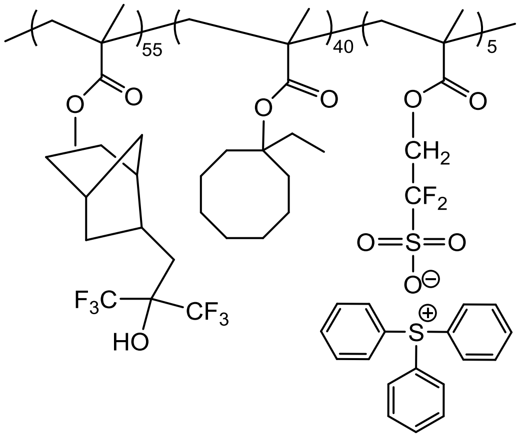
- Low Ea Resists are attractive candidates for high resolution imaging
- Features as small as 20 nm (l/s arrays) can be resolved in KRS
- Water absorption occurs on the same time scale as the deprotection reactions in KRS
- The rate of the deprotection reaction can be controlled by controlling humidity in a post expose delay step
- Relationship between water diffusion, acid diffusion and resolution unclear from indirect measurements
- Controlling humidity conditions after exposure may be a way to optimize resolution in Low Ea resists in E-Beam or EUV
- Blur can show up as chemical flare ?

KRS 24 exposure 11 x 8 dose array no base

Bound PAG's

- Introduction
- Materials
- Characterization
  - Polymer Properties
  - Thermal Stability of Formulations
  - Acid Evaporation
  - Top Down Blur Data
  - Kinetic Data
  - Acid Yield Data
  - Polymer Morphology
- Litho Results
  - Contrast and Dissolution
  - EUV Imaging Performance
- Summary

Bound PAG - Example

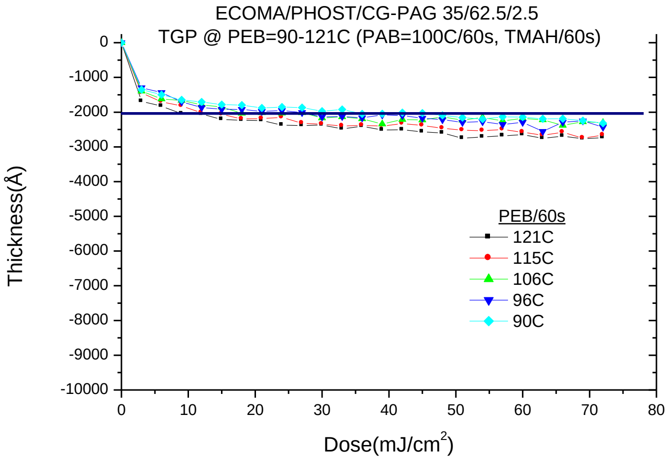


SPIE 2010

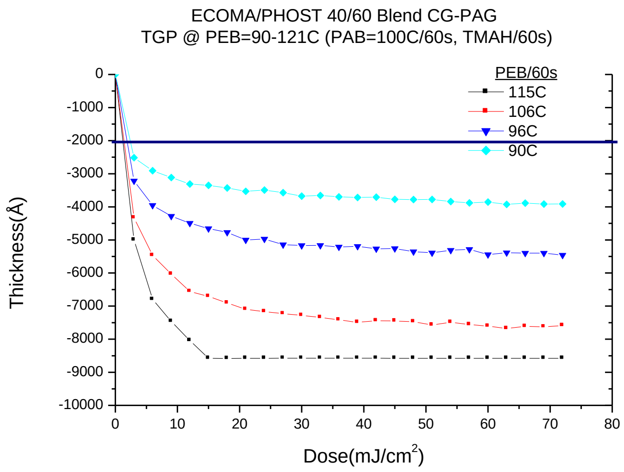
Bound PAG's – Best you can do with respect to Acid diffusion ???

Top Down Image Blur Measurements

Bound-PAG



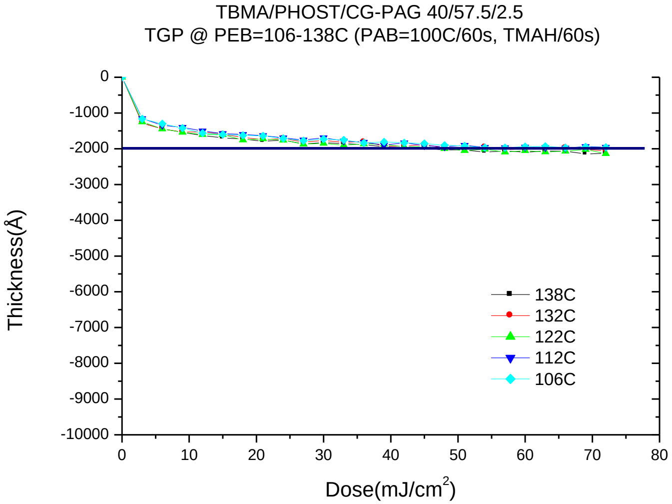
Unbound-PAG



ECOMA ESCAP

Abs 16.1/micron

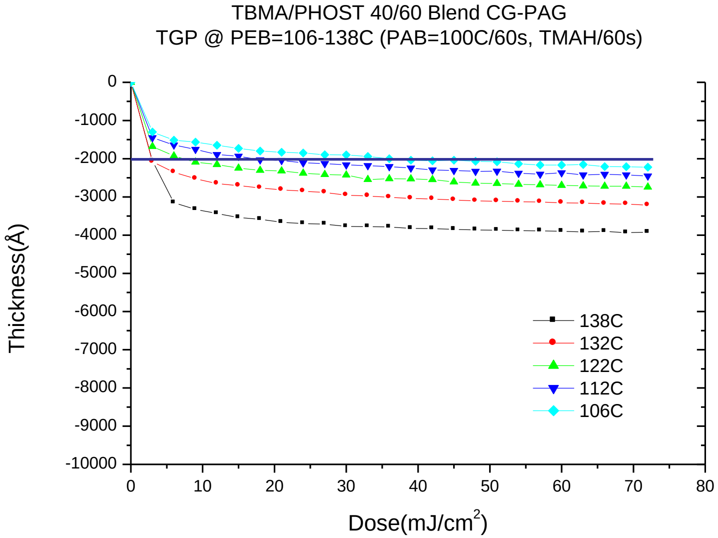
Low Ea



TBMA ESCAP

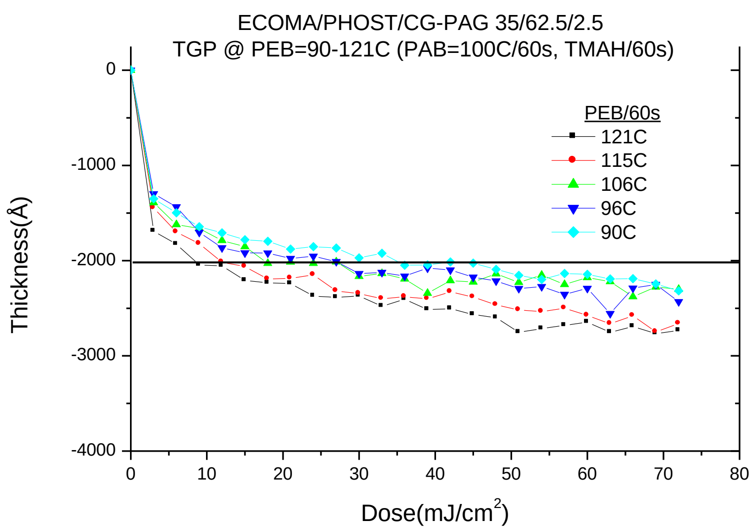
Abs 14.7/micron

High Ea

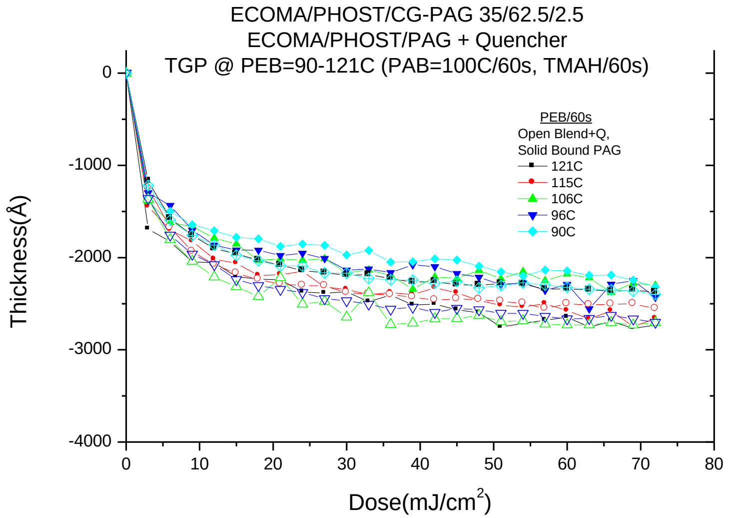


Top down diffusion Measurements - Bound PAG vs. Unbound PAG – Effect of Basic Additives – ECOMA/pHOST polymer backbone

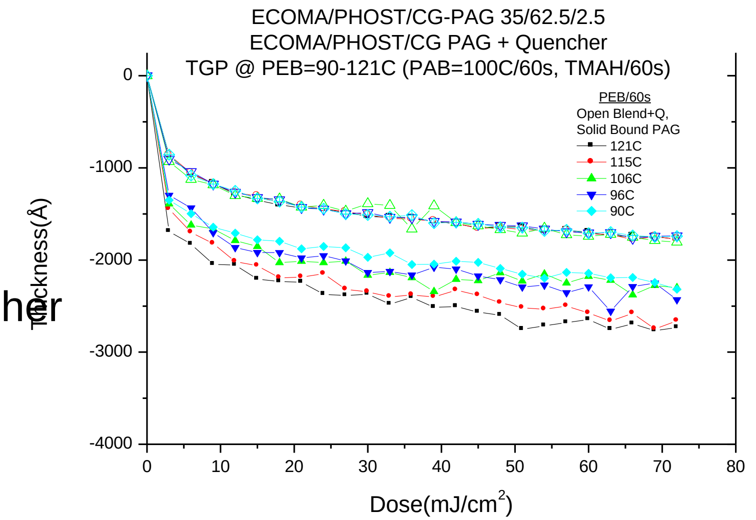
Bound PAG



Bound PAG + BLEND/Quencher



Bound PAG + Bound PAG/Quencher



Comparable diffusion lengths
seen for bound PAG with no quencher
and standard PAG/Quencher Formulation
Lower diffusion (Blur) observed for BPAG/Quencher combination

Summary – Bound PAG

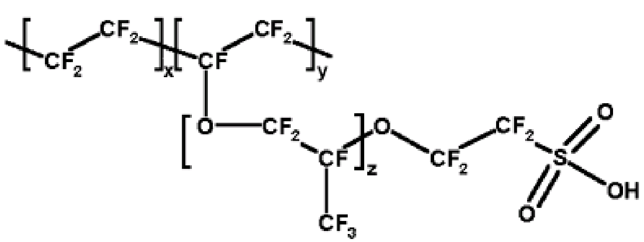
- Decreased long range diffusion observed for bound PAG's vs. PAG blends for all pHOST based systems tested
- Addition of Base quenchers
  - Blend with Base comparable to bound PAG
  - Bound PAG with base – lowest diffusion (Blur)
- Slower reaction rates observed for bound PAG's in ECOMA/NBHFMA and ECOMA/TBMA systems
- Comparable acid yield observed for bound and blend seen in ECOMA/NBHFMA system.
- Lithographic results – ECOMA/NBHFMA system – Bound PAG
  - Eo significantly higher than blend. High PEB bake temperature sensitivity
  - Increased resist swelling, slower dissolution rate for bound PAG
  - Best litho results – Bound PAG + base

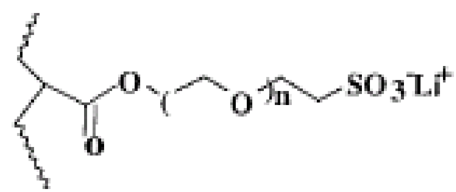
- Possible improvements to Bound PAG resists ?

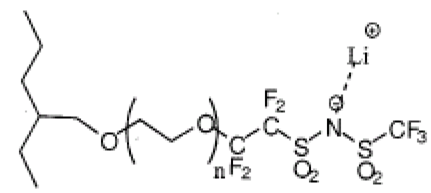
Ionomers

- Ion containing Polymers
  - Ionomers - < 15mol% ionic monomer
  - Polymers whose bulk properties are governed by the presence of ionic aggregates
    - Tg
    - Mechanical Properties
    - Melt Viscosity
    - Transport properties
      - Conductivity
      - Proton transfer
  - Aggregates detectable with SAXS (“Ionomer Peak”)

- Nafion
  - Ion (proton) conduction polymers
  - Sulfonic acids cluster together – form reverse micelles
  - Morphology and proton mobility strongly dependent on water concentration
  - Proton conductivity in Nafion comparable to 0.5 M HCL at high hydration levels (Spry, 2009)
- Polyelectrolyte single-Ion conductors for Lithium Ion battries
  - Conductivities (10-5 S/cm) less than solution
  - Best systems have long side chains, Fluorosulfonate groups
  - High transference numbers
  - Li ion motion simulated with molecular modeling



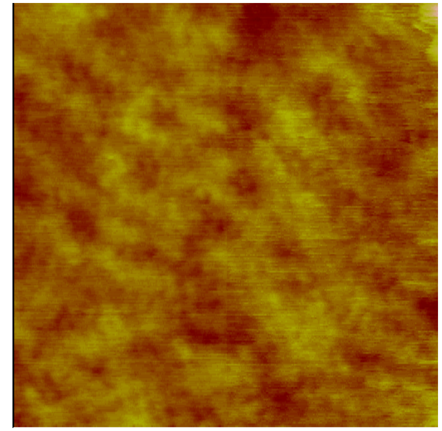




Aggregation in BPAG films ??

- AFM - Characteristic sub-structure with well-packed spherical domains (d: about 10 nm) for polymer bound PAG: Consistent with self-organization of ionic 'block' (PAG unit) in polymer matrix (Allen, et al. Photopolymer 2009)

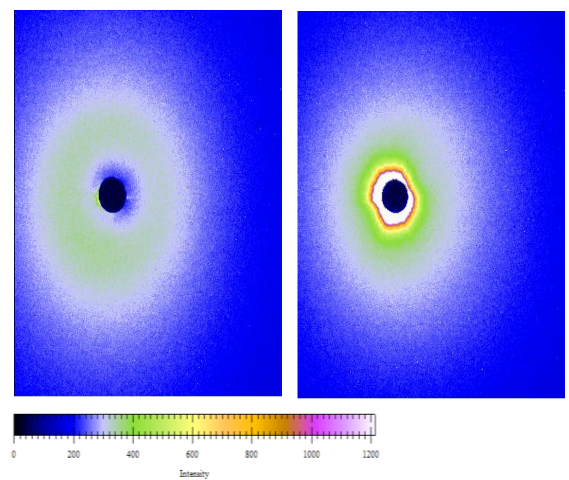
- XRay Analysis
  - Reflectivity – Consistent with a stratified film in the case unbound PAG* – no evidence of this in the case of bound PAG films
  - SAXS analysis – Strong scattering observed in films of bound PAG film consistent with 'Ionomer" peak Correlation length ~ 40-60nm (in thick films)



AFM

Rms: 0.204 nm

Free PAG BPAG



SAXS

L. Bozano SPIE 2011

* Many examples of PAG segregation reported for pHOST and methacrylate systems

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Low Ea resists and bound PAG designed to minimize distortion of the acid latent Image after exposure – is there a way to generate a better image to start with ?

- Contrast Enhancement
  - Aerial Image Shaping

Can imaging chemistry be further manipulated to improve resolution by introducing spatial nonuniformities in reactants?

Base is uniformly distributed

$$\text{acid} + \text{base} \rightleftharpoons \text{neutral}$$

Photo**G**enerated **B**ase is nonuniformly distributed – <u>same</u> profile as acid

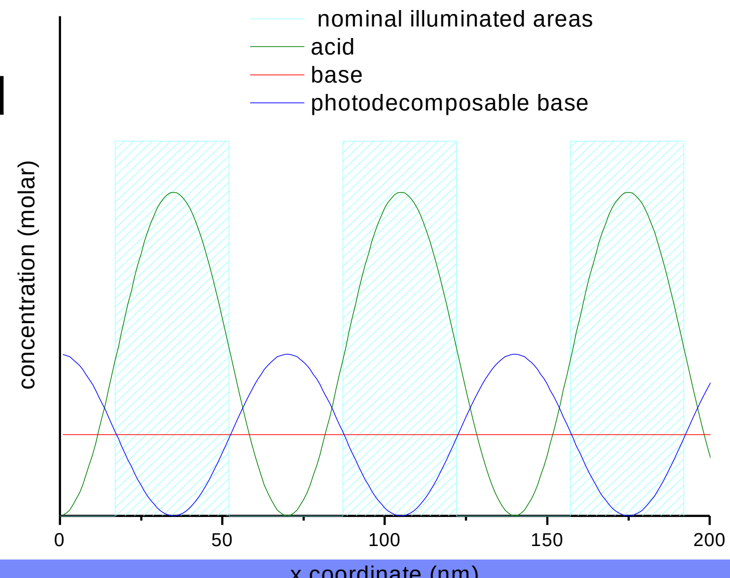
$$\text{acid} + \text{PGB} \rightleftharpoons \text{neutral}$$

Photo**D**ecomposable **B**ase is nonuniformly distributed – profile is <u>complementary</u> to acid

$$\text{acid} + \text{PDB} \rightleftharpoons \text{neutral}$$

Acid **A**mplifier nonlinearly modifies the acid concentration profile

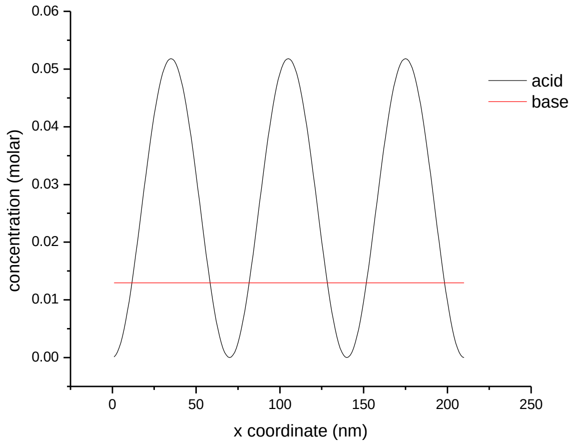
$$\text{acid} + \text{AA} \rightleftharpoons 2\ \text{acid}$$



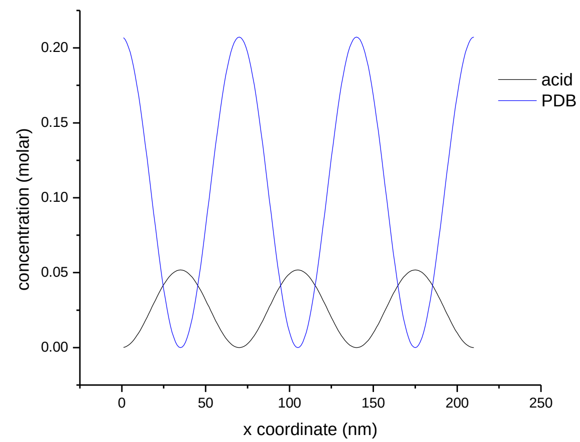
Simulations
VSIM in-house tool based on Gillespie-Bunker stochastic kinetics algorithm
Incorporates chemical kinetics and transport
CA resist PEB model based on experimental measurements; predictions match experiment

Typical concentration profiles at start of PEB

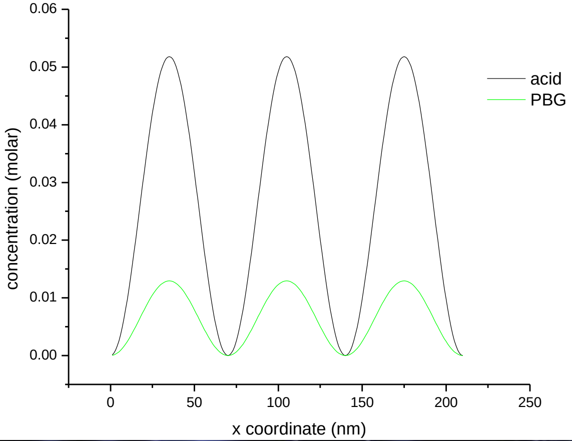
standard acid plus 25% base



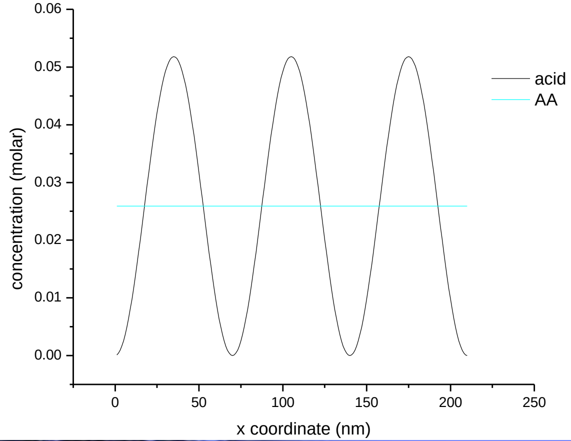
acid plus 400% photo-decomposable base



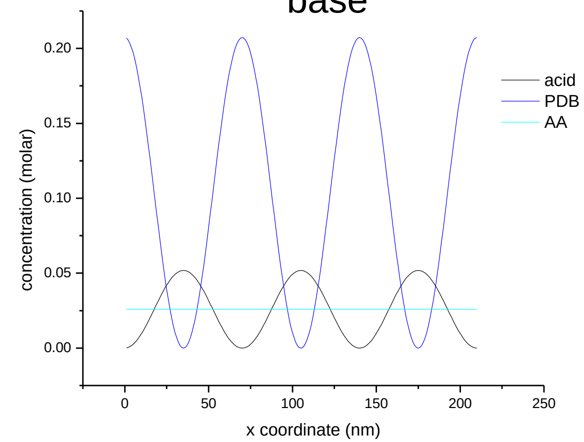
acid plus 25% photo-base generator

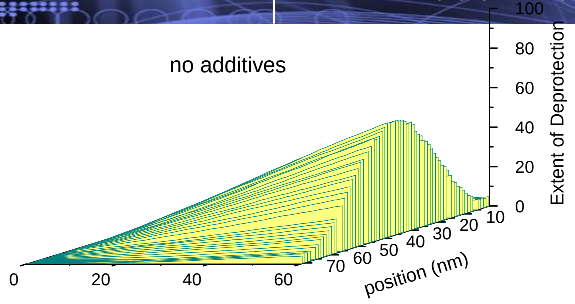


acid plus 50% acid amplifier

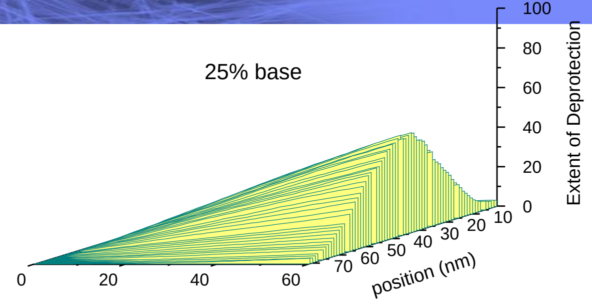


acid plus 50% acid amplifier plus 400% photo-decomposable base

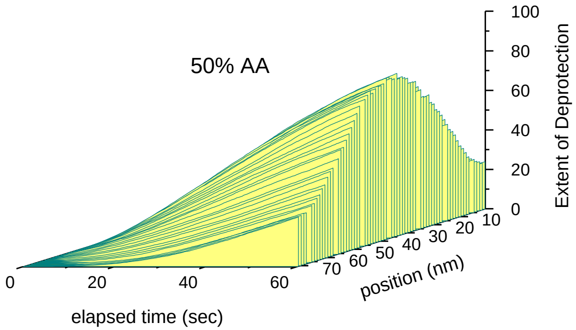




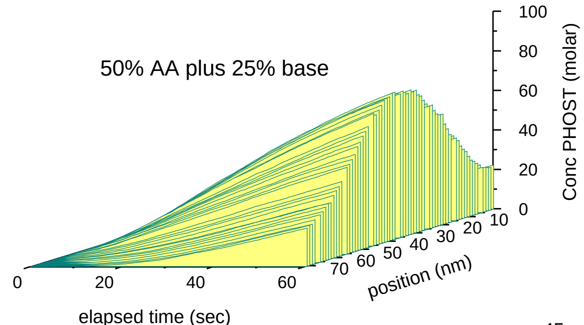
(a)



(b)



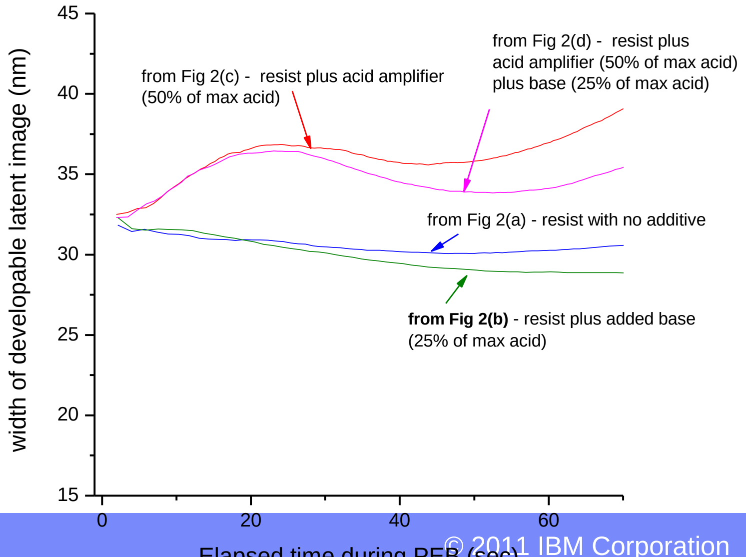
(c)

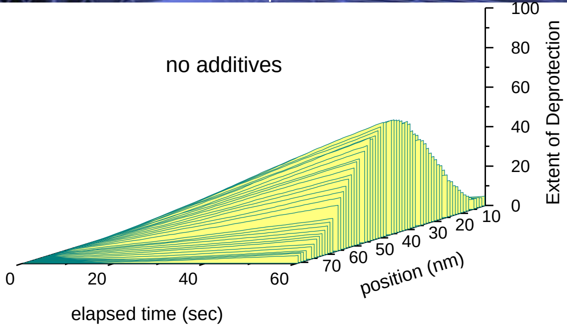


(d)

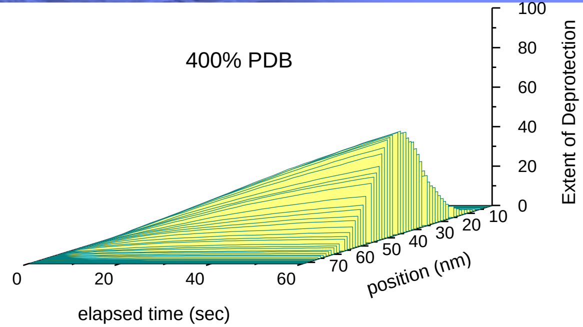
Profile plots – extents of deprotection vs time

Plot of linewidths vs time

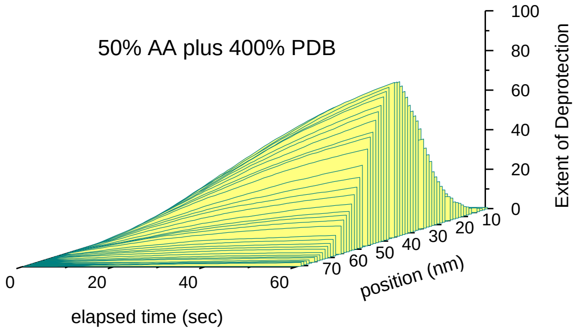




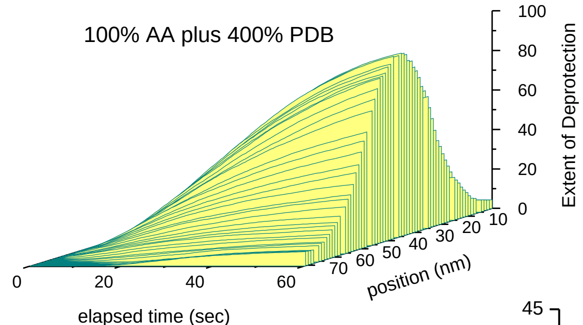
(a)



(b)



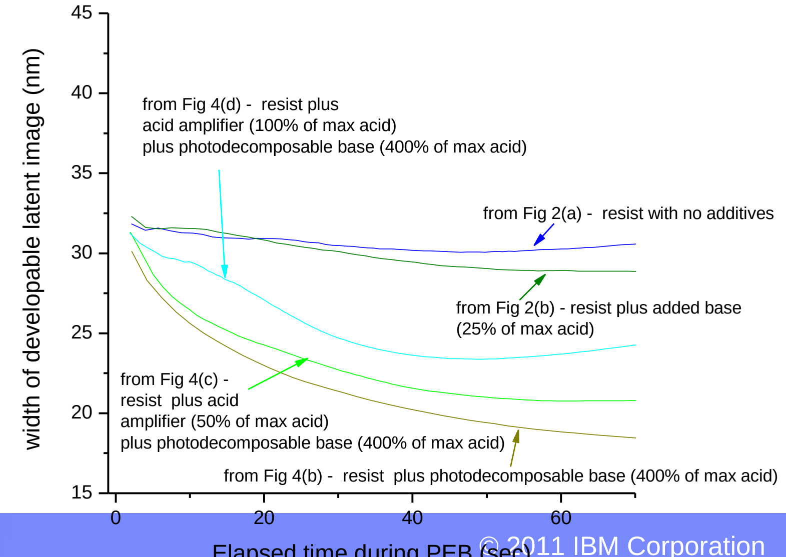
(c)



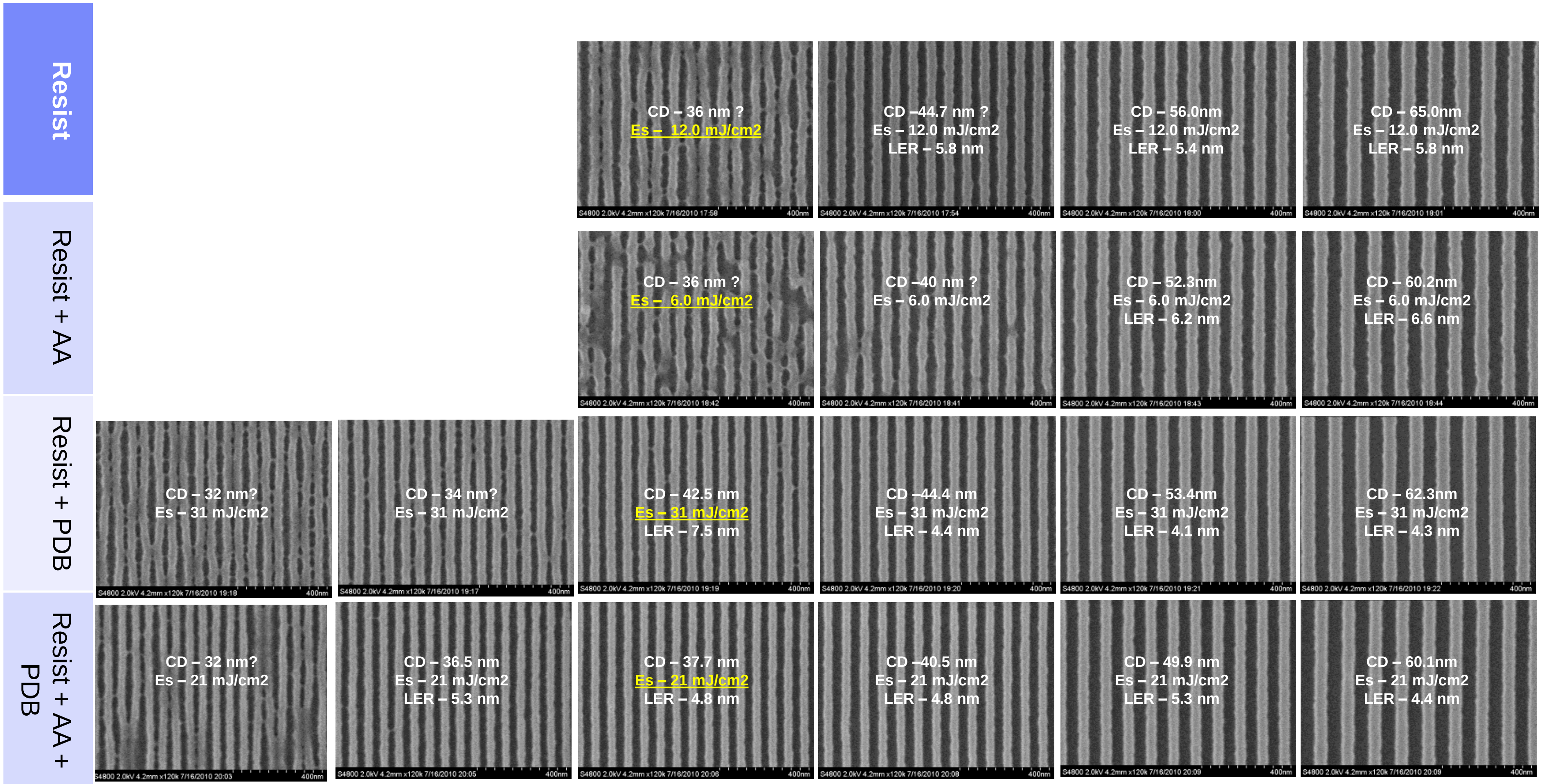
(d)

Profile plots – extents of deprotection vs time

Plot of linewidths vs time

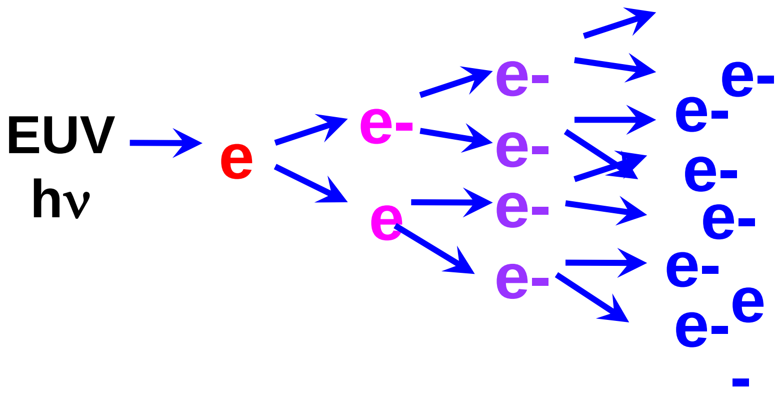


AIS Resist I (Resist With AA & PDB): EUV Imaging

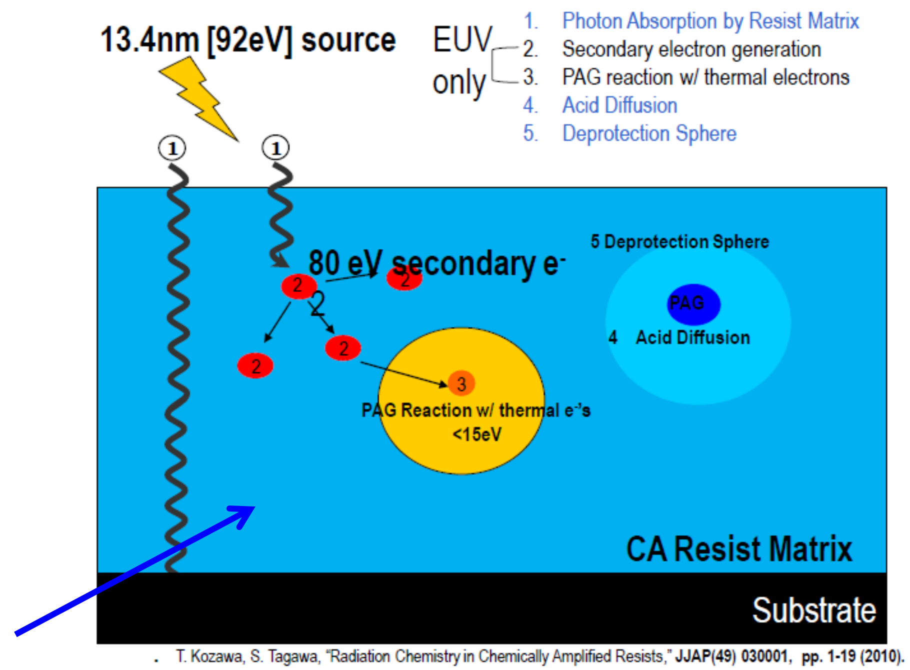


Substrate – BARC ; FT – 63 nm; PAB – 110 C/60 s; Exposure – EUV (Annular); PEB- 110 C/60s; Dev – 30s; CD&LER Calculated Using SuMMIT

Secondary electrons in EUV



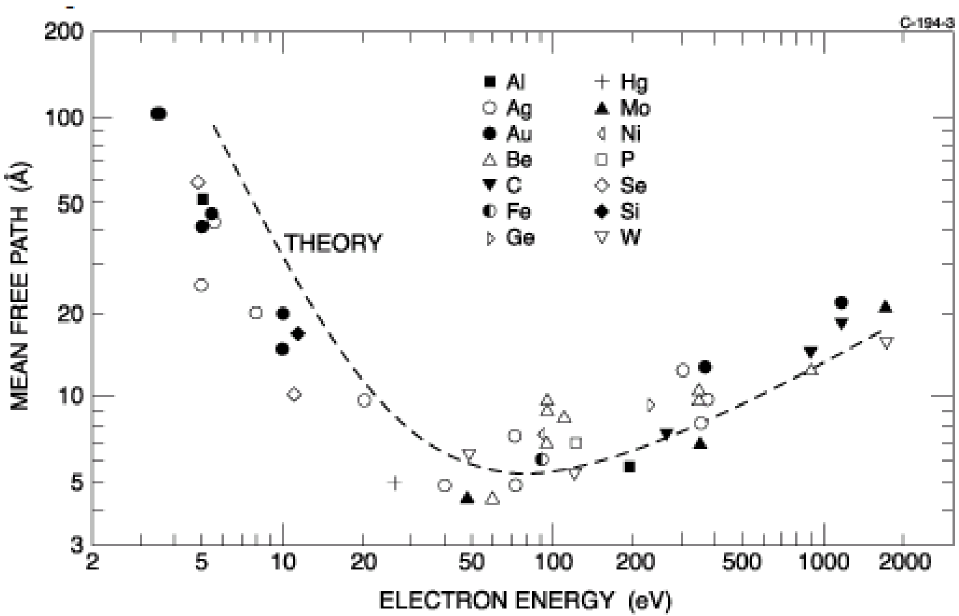
Film Quantum Yield ~ 2 – 6
Higgins et al JJAP 2011



Thackeray Plenary Lecture SPIE, 2011

R. Brainard U at Albany

Secondary Electron Yield - Physics



The main results are: the majority of secondary electrons photoemitted under 13.5 EUV photon irradiation by each resist have energies less than 10 eV, and a small fraction have energies up to ~ 20eV. The total SEY depends on photon energy, and is ~ 0.02 at 13.5 nm.

Yakshinskiy et al International Symposium on EUV 2009

P. Hoffman Surface Science Online (http://www.philiphofmann.net/surflec3/index.html)

Thermalization distance significantly longer than the inelasic mean free path of 20 – 100 eV electrons
Kozawa, Tagawa JJAP 2010

Secondary Electrons – Resist Chemistry

$$\left((9.7\,nm)^2 + (4.3\,nm)^2 + (2.5\,nm)^2 + x^2\right)^{1/2} = 11.5\,nm$$

$$x = 3.7\,nm$$

- ArF acid blur
- Polymer Radius of Gyration
- Secondary electron blur
- Unaccounted for blur-- flare, OOB?

The extracted blur kinetics display perfectly linear Arrhenius behavior, indicating that there is no sign for secondary electron blur at 22-nm half pitch. At the lowest PEB setting the total blur length is ~4 nm, indicating that secondary electron blur should be well below that

Gronheid et al J. Micro/Nanolith. 2011)

Thackeray SPIE, February 2011

Thackeray, James W.; Wagner, Mike; Kang, Su Jin; Biafore, John. Journal of Photopolymer Science and Technology (2010),

Determination of the optimum thermalization distance –
3 nm for 11 nm ½ pitch

Kozawa,Tagawa J Photopolymer Sci. Technol 2011

Inorganic resists

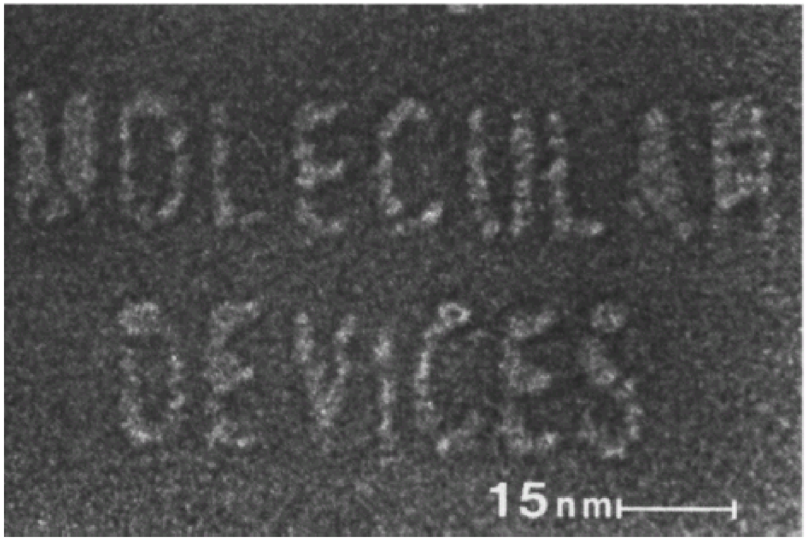


FIG. 6. Patterns etched into NaCl crystals supported on a 5–10 nm carbon substrate. (a) The average height of the characters (e.g., *a*, *w*, etc.) is 10 nm and the linewidth is approximately 1.5 nm. The quotation is from Lessing. (b) The average height of the characters is 16.7 nm and the linewidth is about 2.0 nm.

Isaacson,Murray JVST 1981

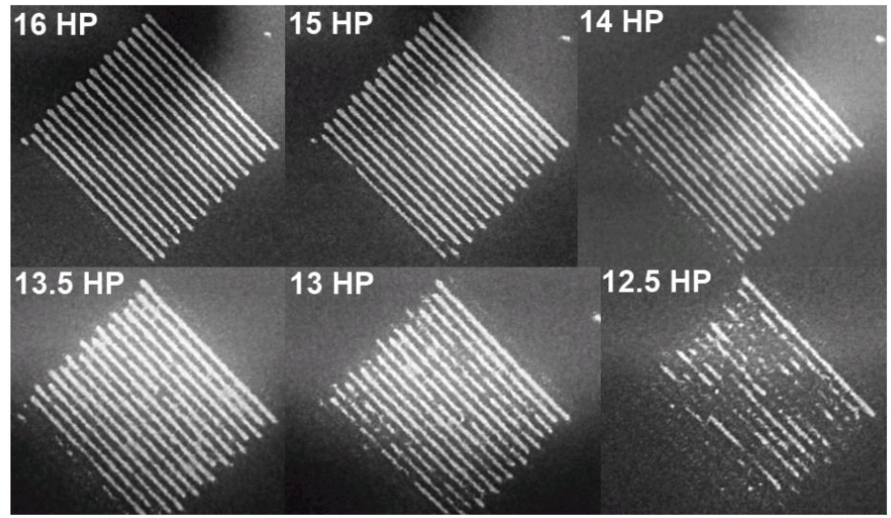
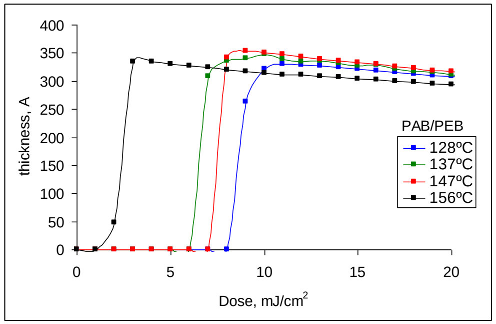


Figure 2. 16 nm HP – 12 nm HP lines produced by F2X mode on the SEMATECH-Berkeley MET with XE15AB resist at 70 mJ/cm^2. The 16-nm HP lines printed at 13-nm CD, and they have a LER of 2.0 nm.

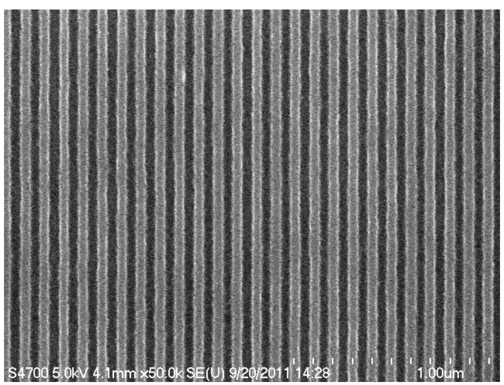
Stowers et al SPIE 2011

New IBM Inorganic Resists — 1st Imaging Results

Contrast and Imaging at 193 nm

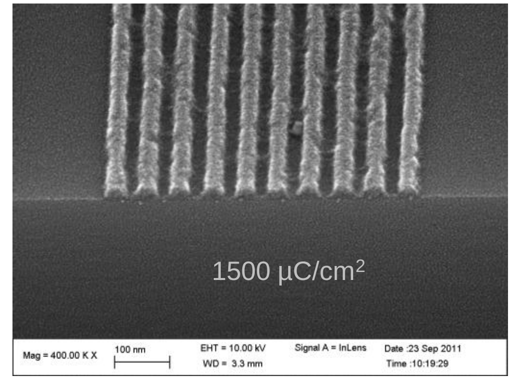


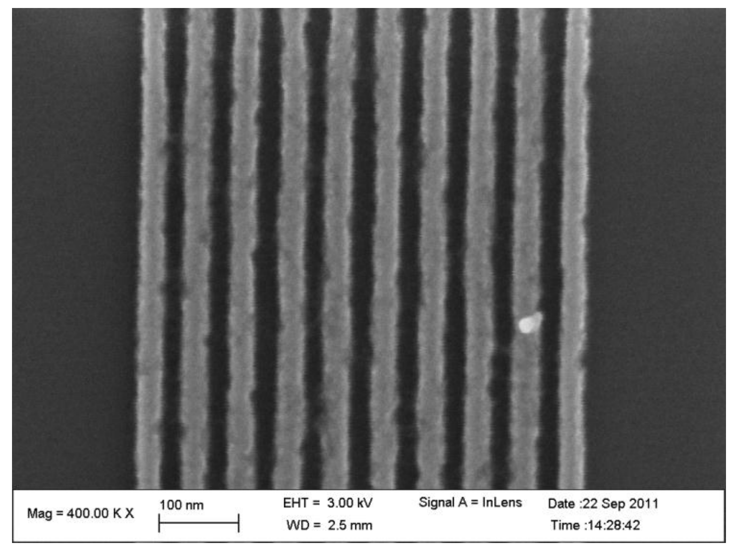
193 nm "IL Exposure" - 50 nm



9.55 mJ/cm2

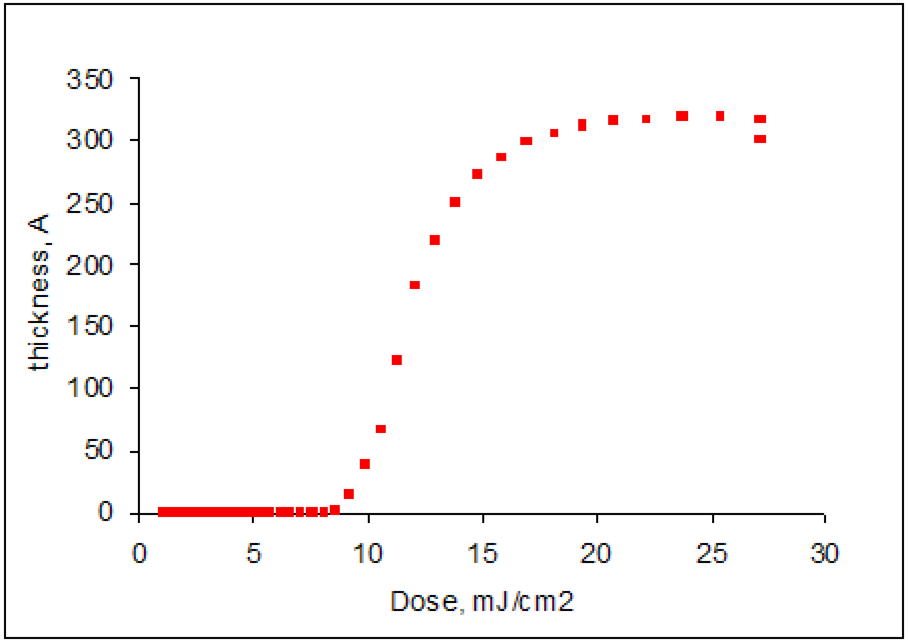
E-Beam (30 nm)

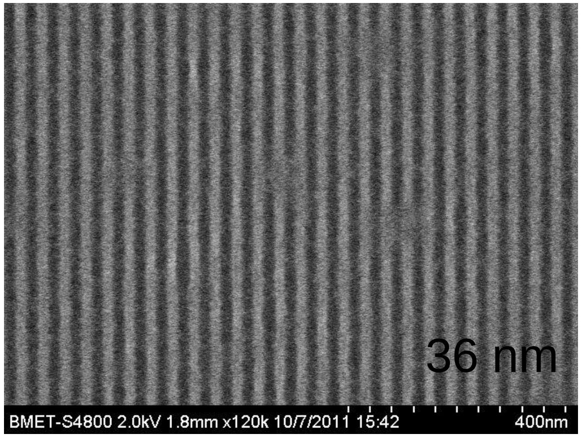


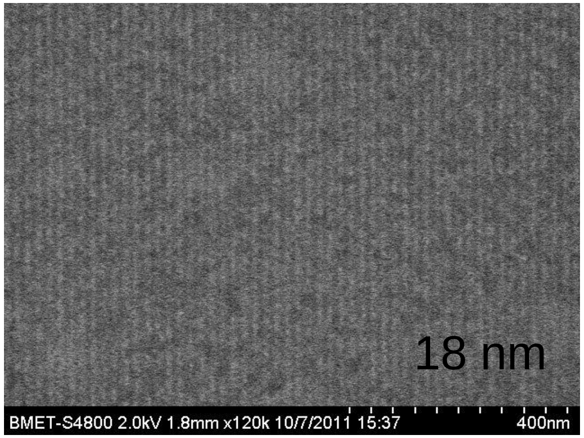


1St EUV exposures

- Outgassing – Only CO, CO_2 observed in significant amounts







35 mJ/cm2 LBNL

J. Bass, H Truong IBM

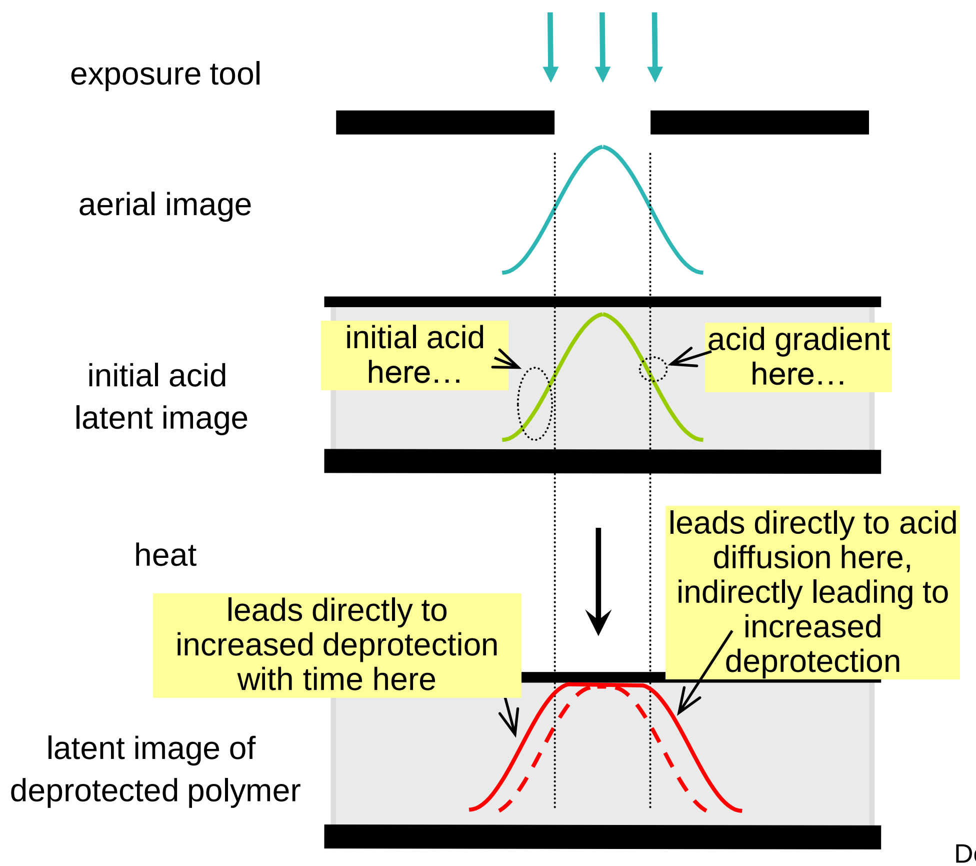
Summary

"This latter result indicates not only that the PC XT-driven STEM is producing reliable exposure distribution data, but also that t-BOC has approximately the same resolution as PMMA, even though its sensitivity can be six times higher. These results suggest that resolution may be limited by something inherent in all organic resists, such as, perhaps, the range over which low-energy secondary electrons are created by high-energy electrons"

The End

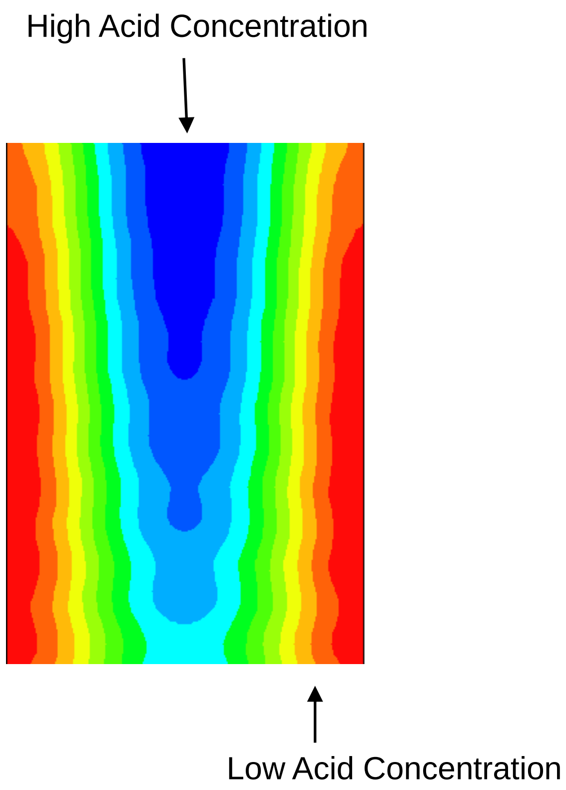
- Acknowledgements
  - Colleagues at IBM especially H. Truong, S. Swanson, P. Brock,B.Davis, K. Petrillo, Y.-H Na, H.-C Kim, W. D. Hinsberg, L. Sundberg, R. D. Allen,
  - Colleagues at IBM's Partners
  - Helpful discussions with R. Tromp, A. Brodie, R. Bartynski, R. Brainard, M Guillorn

Image Blur



Photochemical Image –

Photoacid profile in resist film



Deprotection in nominally unexposed areas near the line-edge, a consequence of small amounts of photogenerated acid produced by diffracted and scattered light, can lead to line narrowing that in many aspects mimics the effects of acid diffusion. Hinsberg SPIE 2004